

ANODIC GROWTH OF ANTIMONY OXIDE FILMS

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Antimony is used as an alloying additive in lead alloys for grids in lead-acid batteries. It has also received some attention due to the use of antimony oxide as a photoconductor material, although its duration is low due to corrosion.

Previous studies on the formation and properties of antimony oxide in different solutions has been limited to low potentials [1-3]. Also, the dissolution behaviour of the anodic film formed in phosphate solutions has been studied by impedance measurements [4].

In this work the anodic growth of antimony oxide films electroformed under potentiodynamic or galvanostatic conditions as well as their stability in the formation electrolyte were studied. Antimony oxide films of different thickness were grown potentiodynamically or galvanostatically up to different potential values in alkaline, neutral or acidic solutions of different concentration and pH. The working electrode consisted of a polycrystalline antimony rod (99.999% purity) polished mechanically with emery paper and diamond paste (9 μm). After the mechanical polishing, an oxide layer was grown and then the electroformed film was dissolved chemically in a 1M HCl solution. The procedure was repeated several times until a reproducible j/E potentiodynamic profile was obtained. Ellipsometry in situ was used as a monitoring technique during the anodic growth of the anodic oxide films as well as at the open circuit potential in the formation electrolyte for studying the dissolution process. Ellipsometric measurements were made in a Rudolph Research 2000 FT rotating analyzer automatic ellipsometer. The wavelength employed was 546.1 nm with the incident light beam at 70°.

The j/E potentiodynamic profiles show during the positive potential scan three main anodic current peaks in the -1.5 to 0V potential range, which are attributed to the formation of a layer containing Sb(III) species through a complex mechanism in three stages [1]. After this region, the current density reaches an approximately constant value and increases again up to define another potential region of stationary current at potentials exceeding *ca.* 3-4 V. These two regions of steady state current density are associated with the anodic growth of two different antimony oxides. The anodic film is a good insulator for anodic reactions up to *ca.* 9.5 V where a sharp current increase with simultaneous gas evolution, which corresponds to the oxygen electroformation reaction, is observed. On the reverse sweep, the current density falls and the growth rate decreases. The negative sweep also shows the electroreduction of the electroformed film before the hydrogen evolution reaction, which occurs on the electroreduced metal surface. From experiments applying combined repetitive sweeps with potential holdings, it can be deduced that there is a noticeable chemical dissolution of the film. The constant current regions during the growth implies no change in the potential drop across the oxide-electrolyte interface and,

hence, the total change of potential falls across the film [5]. This indicates that at high potentials the growing occurs through a mechanism of ionic migration under a high field. The potential/time curves during galvanostatic oxide growth also present a break in the 3-4 V range, indicating the growth of two oxide layers of different properties. In this case the growing potential can be higher than in potentiodynamic experiments.

The ellipsometric data obtained during the anodic growth allow us to obtain the optical constants of the layers as well as the film thickness from which the growing field can be characterised. Also, the rate for the dissolution processes can be obtained.

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